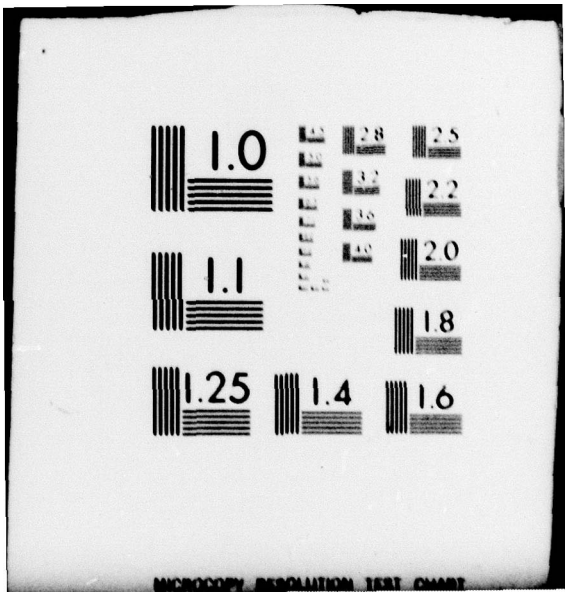
AD-A073 641 OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY F/G 20/2
THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIMETHYLTIN CHLORIDE AT--ETC(U)
AUG 79 M B HOSSAIN, J L LEFFERTS, K C MOLLOY N00014-77-C-0432

UNCLASSIFIED TR-8 NL

| OF |
AD
A073641

END
DATE
FILMED
10-79
DDC


1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART

AD A073641

AD A067222

DDC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 8	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): The Crystal and Molecular Structure of Trimethyltin Chloride at 135K. A Highly Volatile Organotin Polymer.	5. TYPE OF REPORT & PERIOD COVERED: 10
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): M. Bilayet Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm, J.J. Zuckerman	8. CONTRACT OR GRANT NUMBER(s): N00014-77-C-0432
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Oklahoma, Department of Chemistry, Norman, Oklahoma 73019	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 053-636
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of Navy, Arlington, Virginia 22217	12. REPORT DATE: 27 August 1979
	13. NUMBER OF PAGES: 8
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office): TR-8	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

Technical rept.,

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for Publication in Inorganic Chimica Acta

DDC RECEIVED SEP 11 1979 A

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Trimethyltin Chloride, Structure, X-ray, Crystal and Molecular Structure, Organotin, Polymer, Association, Chlorine Bridging, Volatile Polymer, One-Dimensional Polymer, Low-Temperature X-ray Study, Linear Polymer.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Trimethyltin chloride consists of planar trimethyltin units associated into a linear polyneer by bent chlorine bridges.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

403 980

P-1

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-636

TECHNICAL REPORT NO. 8

The Crystal and Molecular Structure of Trimethyltin Chloride at 135K. A Highly Volatile Organotin Polymer.

by

M. Bilayet Hossain, J.L. Lefferts,
K.C. Molloy, D. van der Helm, and
J.J. Zuckerman

Prepared for Publication

in

Inorganic Chimica Acta

University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019

STATEMENT

Trimethyltin chloride is the key starting material in the laboratory synthesis of the trimethyltin derivatives most subjected to study. It is an article of commerce, and has itself been extensively studied by a great variety of spectroscopic and physical methods. There is in the literature starting in 1970 a trail of oft referenced private communications (see our ref. 17) which describe a yet unpublished X-ray structure which is incorrect. In addition, the structure of the analogous triphenyltin chloride, which is monomeric at ambient temperature, is said to undergo a change on cooling to a chlorine-bridged polymer, but this suggestion is based upon NQR data at 77K which cannot be reproduced (see our ref.5). The structure of the homologous trimethyltin fluoride cannot be solved because of disorder, and thus the widely-quoted bridging halide structures for R_3SnX compounds are being confirmed here in the case of the title compound for the first time.

The Crystal and Molecular Structure of Trimethyltin Chloride at 135K. A Highly Volatile Organotin Polymer.

M. BILAYET HOSSAIN, J.L. LEFFERTS, K.C. MOLLOY, D. VAN DER HELM* AND J. J. ZUCKERMAN*

Department of Chemistry, University of Oklahoma, Norman, OK 73019 (U.S.A.)

Trimethyltin chloride is a key laboratory starting material and has been studied extensively by spectroscopic methods, yet the solid state structure of this highly toxic, low melting 9m. 39.5°C.), volatile (b. 154°C.) material has never been determined because of experimental difficulties. The structure of the homologous trimethyltin fluoride,[1] which is associated through bridging fluorines, is perhaps the most widely quoted organotin structure of all,[2] yet disorder within and between the -F-Sn-F-Sn- chains prevents a satisfactory solution to the anomalous electron density projections recorded at ambient temperatures.[3] Triphenyltin chloride[4] and bromide,[5] on the other hand, exist as discrete, monomeric molecules in the crystal.[6]

Crystals of trimethyltin chloride are monoclinic,

$a = 12.541(8)$, $b = 9.618(11)$, $c = 11.015(11)$ Å, $\beta = 92.62(7)°$, space group P2, and $Z = 2$. Each asymmetric unit consists of four molecules. The structure was solved from 2183 independent reflections [$2\theta \leq 53°$, Mo K_α radiation $I > 2\sigma(I)$] recorded at 135± 2K on a Nonius CAD-4 counter diffractometer by the heavy-atom technique, and refined to a final R value of 0.069 (weighted = 0.058). Sublimation of the crystals prevented the measurement of all faces, and thus no corrections for absorption could be made. The calculated density is 1.994 g/cm^3.

The stereochemistry of the asymmetric unit is shown in the Figure, along with mean values of the bond distances and angles. The two tin-chlorine distances are not equivalent, with the intramolecular bond [mean value 2.434(5,18)Å][10] considerably shorter than the intermolecular [mean value 3.259(5,11) Å], although the latter is significantly shorter than the sum of the respective van der Waals radii (3.85 Å).[11] Comparison with the parameters of the recent gas-phase electron diffraction study[12] is shown in the Table along with data from the analogous $[(CH_3)_3SnCl_2]^-$ anion (gegen ion $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+$) which takes an axially distorted, trigonal bipyramidal structure with one Sn-Cl the longest such intramolecular distance yet reported.[13]

The Cl-Sn-Cl-Sn-fragment is nearly linear at tin

[mean Cl-Sn-Cl angle 176.8(2,3)°],[10] but bent at chlorine [mean angle 150.9(45)°], imposing a zig-zag character to the polymeric backbone, as in trimethyltin methoxide. However, in the latter case the trimethyltin moieties are staggered [the methoxyl methyl group eclipses an intermolecularly attached $(CH_3)_3Sn$ methyl][14], while the trimethyltin units in the $(CH_3)_3SnCl$ chain are eclipsed. Single -Sn-Cl-Sn-bridges such as those found here may also appear in the structure of diphenyltin dichloride[15] which has been reinterpreted in terms of chlorine asymmetrically bridging four- and six-coordinated tin atoms (intra- 2.353, inter- 3.78 Å).[16]

The intermolecular tin-chlorine association in $(CH_3)_3SnCl$ is apparently disrupted on melting or dissolving in carbon disulfide, as shown by reduced infrared and Raman ν(Sn-Cl) values.[17,18]

Acknowledgement. Our work is supported by the Office of Naval Research (JJZ) and the National Cancer Institute, DHEW, CA 17562 (DvdH).

References and Notes

1 H.C. Clark, R.J. O'Brien and J. Trotter, J. Chem. Soc., 2332 (1964).

2 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24, 251 (1978).

3 K. Kasuda, Y. Kawasaki, N. Kasai and T. Tanaka, Bull. Chem.

Soc. Jap., 38, 1216 (1965).

4 N.G. Bokii, G.N. Zakharova and Y.T. Struchkov, J. Struct. Chem. USSR, 11, 828 (1970).

5 H. Preut and F. Huber, Acta Cryst., B35, 744 (1979).

6 The suggestion of a phase transition occurring in triphenyltin chloride between ambient and liquid nitrogen temperatures[4] is based upon a very low value reported for the NQR coupling constant at 77K.[7] However, this signal could not be reproduced by later workers.[8] The close similarity of the Mössbauer parameters at 80, 110 and 295K strongly suggest that triphenyltin chloride is isostructural over this temperature range.[9]

7 T.S. Srivastava, J. Organomet. Chem., 10, 373 (1967).

8 N.W.G. Debye and M. Linzer, J. Chem. Phys., 61, 4770 (1974).

9 G.M. Bancroft, K.D. Butler and T.K. Sham, J. Chem. Soc., Dalton Trans., 1483 (1975).

10 Figures within parentheses refer to the standard deviation of a single observation and the r.m.s. deviation of the four independent measurements, respectively.

11 A. Bondi, J. Phys. Chem., 68, 441 (1964).

12 B. Beagley, K. McAloon and J.M. Freeman, Acta Cryst., B30, 444 (1974).

13 P.J. Vergamini, H. Varenkamp and L.F. Dahl, J. Am. Chem. Soc., 93, 6327 (1971).

14 A.M. Domingos and G.M. Sheldrick, Acta Cryst., B30, 519 (1974).

15 P.T. Greene and R.F. Bryan, J. Chem. Soc., (A), 2549 (1971).

16 N.G. Bokii, Yu. T. Struchkov and A.K. Prokofiev, J. Struct. Chem., USSR, 13, 619 (1972).

17 H. Kriegsmann and S. Pischtschan, Z. Anorg. Chem., 308, 212 (1961).

18 Reports of an earlier X-ray structure by A.G. Davies, H.J. Milledge and D.C. Puxley showing a five-coordinated structure bent at tin have been quoted in the literature,[19] but never published.

19 N.W. Alcock and J.F. Sawyer, J. Chem. Soc. Dalton Trans., 1090 (1977); M.T.P. Internat. Rev. Sci., 4, 280 (1972); R.V. Parish and R.H. Platt, Inorg. Chim. Acta, 4, 65 (1970).

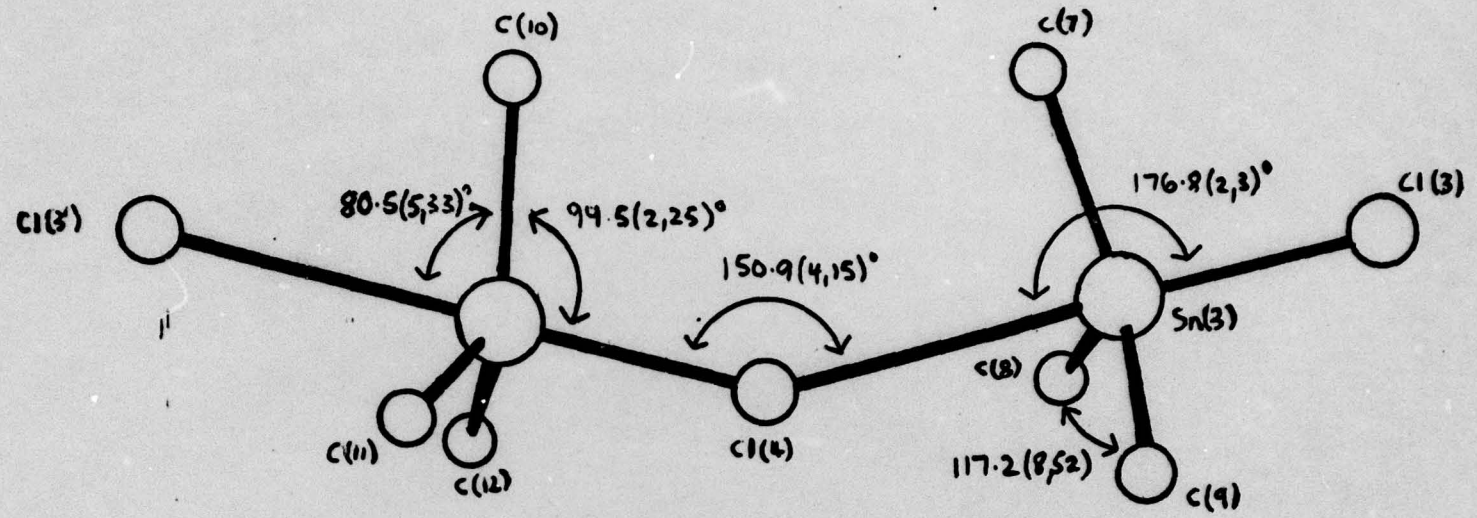
Table

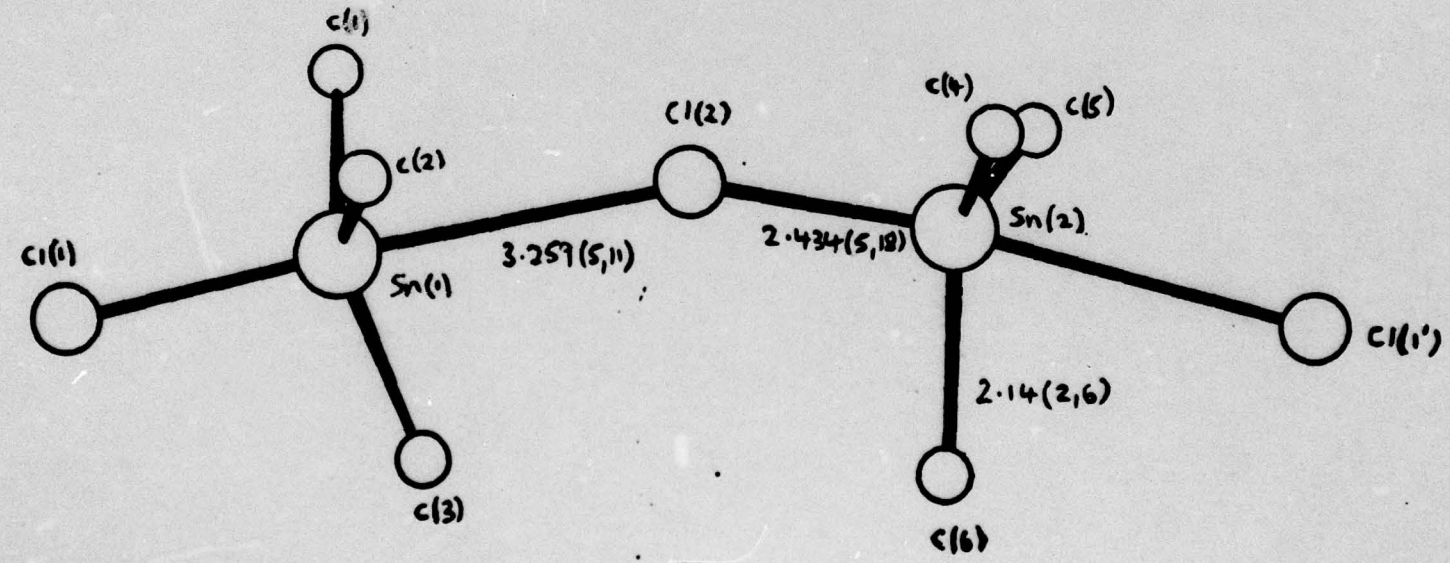
	d(Sn-C)	d(Sn-Cl)	<C-Sn-C	<C-Sn-Cl	d(Sn---Cl)	<(Cl-Sn---Cl)
$(CH_3)_3SnCl$[a] X-ray at 135K	2.14(2,6)Å	2.434(5,18)Å	117.2(8,52)°	99.5(5,25)°intra- 80.5(5,33)°inter-	3.259(5,11)Å	176.8(2,3)°
predicted[b]	--	--	118°	99°	3.54	--
e.d. at 90°C[c]	2.106±0.006	2.351±0.007	114.9±1.6°	103.2±0.6°	--	--
$[(CH_3)_3SnCl_2]^-$ X-ray at R.T.[d]	2.12	2.572(4) 2.696(3)	--	--	--	--

[a] This work.
[b] R.F. Zahrobsky, J. Solid State Chem., 8, 101 (1973).
[c] Ref. 12
[d] Ref. 13

Figure Caption

The asymmetric unit in the trimethyltin chloride structure. The interchain d(Sn....Cl) values are greater than 4.1Å.


C(10)
C(7)
Cl(5)
80·5(5,33)°
94·5(2,25)°
176·8(2,3)°
Cl(3)
150·9(4,15)°
Sn(3)
C(8)
C(11)
C(12)
Cl(4)
117·2(8,52)
C(9)


C(4)
C(5)
C(1)
Cl(2)
C(2)
Sn(2)
Cl(1)
3·259(5,11)
2·434(5,18)
Sn(1)
Cl(1')
2·14(2,6)
C(3)
C(6)